

# Druckexemplar<sup>15</sup>

Further alkyltin catalysts:

Comparative Example 1g (Tributyltin (2-ethylhexanoate)):

5 A three-necked flask equipped with mechanical mixer, heating, thermometer and vacuum distillation bridge was, under nitrogen protective atmosphere, filled with 149 g (0,25 Mol) hexabutyldistannoxane and 72,1 g (0,5 Mol) 2-ethylhexanoic acid. The reaction mixture was heated up on 80°C. To separate from the reaction water a vacuum of 1  
10 mbar was applied, and the reaction mixture was stirred another 1 h at this temperature.

Yield: 209,8 g (theoretical. 212,1 g) a clear, bright liquid.

Elemental analysis: Sn content = 27,8 %.

15 The production of the examples and comparative examples 1h to 1n followed the same procedure.

Comparative example 1h: Dibutyltin bis(2-ethylhexanoate)

20 Comparative example 1i: monobutyltin tris(2-ethylhexanoate)

Comparative example 1j: dibutyltin pinacolate

Comparative example 1k: monoocetylstannoic acid

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Comparative example 1l: monobutylstannoic acid

Comparative example 1m: monoocetyltin tris(2-ethylhexanoate)

**Comparative example 1n: monododecyltin tris(2-ethylhexanoate)**

**Example 2: Catalyst test by synthesis of a resin for powder coatings:**

5 Starting materials, quantities:

terephthalic acid 83,07 g [0,50 mol]

10 neopentyl glycol (2,2-dimethyl-1,3-propandiol)  
104,15 g [1,00 mol]

catalyst: 0,05 %[m/m] (as metal)

Synthesis:

15 Catalyst, neopentyl glycol and terephthalic acid were given into a 250 ml three necked round bottom flask. The mixture was heated to a maximum by the means of a heating mantel and the reaction water was distilled off and the amount was measured.

20 The reaction time equals the time between the first water formation and the "clear point" of the reaction.

25 Table 1 shows the acceleration of the reaction time in the described resin synthesis with the mixtures of examples 1a, 1b, 1c, 1d, 1e, 1f in comparison with the uncatalyzed reaction or with monobutyltin oxide (0,05 % [m/m]) as catalyst.

Table 1: Reaction time of the mixtures a-f in comparison.

|                              | Volume H <sub>2</sub> O [ml]: |           |           |           |           |           |            |            |            |            |            |            |                       | [min]               |  |
|------------------------------|-------------------------------|-----------|-----------|-----------|-----------|-----------|------------|------------|------------|------------|------------|------------|-----------------------|---------------------|--|
| Catalyst<br>(0,05% as<br>Sn) | 15<br>min                     | 30<br>min | 45<br>min | 60<br>min | 75<br>min | 90<br>min | 105<br>min | 120<br>min | 135<br>min | 150<br>min | 165<br>min | 180<br>min | Reac-<br>tion<br>time | Remarks             |  |
| Without catalyst             |                               |           |           | 1         |           | 1         |            | 2          |            | 3          |            | 4          | 300                   | aborted             |  |
| monobutyl-tinoxide           |                               | 7         |           | 9         |           | 12        |            | 15         |            | 17         |            | 19         | 180                   | Clear,<br>colorless |  |
| 1a                           |                               | 7         |           | 10        |           | 18        |            |            |            |            |            |            | 90                    | Clear,<br>colorless |  |
| 1b                           | 3                             | 6         | 5         | 9         | 11        | 14        |            |            |            |            |            |            | 90                    | hazy,<br>colorless  |  |
| 1c                           | 4                             | 4         | 10        | 14        | 16        |           |            |            |            |            |            |            | 75                    | Clear,<br>colorless |  |
| 1d                           | 3                             | 6         | 10        | 12        | 14        | 16        |            |            |            |            |            |            | 90                    | Clear,<br>colorless |  |
| 1e                           | 3                             | 5         | 6         | 8         | 9         | 10        | 13         | 15         | 18         |            |            |            | 135                   | Clear,<br>colorless |  |
| 1f                           | 3                             | 5         | 7         | 10        | 12        | 14        | 15         | 16         | 18         |            |            |            | 135                   | Clear,<br>colorless |  |

5 Example 3: Catalytically active Sn-compounds with A = alcoholate:

Example 3o: Product of the reaction of monobutyl stannic acid with Ti(OBu)<sub>4</sub> (molar ratio 4 : 1):

10 51,1 g (0,15 mol) Ti(OBu)<sub>4</sub> and 25,3 g (0,60 mol) monobutyl stannic acid were dissolved in xylene (250 ml) and refluxed under a nitrogen atmosphere in a 500 ml three necked round bottom flask for 4 hours. The product was obtained after the solvent was removed under reduced pressure in an amount of 149,6 g (theoretical. 131,9 g) as a yellow solid

15 (Elemental analysis: Sn content = 46,5 %, Ti content = 4,9 %).

Table 3. Polycondensation of BHET with Sb and Ti catalysts.

| catalyst            | temperature<br>[°C] | time<br>[min] | catalyst conc.<br>[ppm] | P <sub>n</sub> |
|---------------------|---------------------|---------------|-------------------------|----------------|
| antimony triacetate | 270                 | 30            | 190                     | 25             |
| antimony triacetate | 270                 | 60            | 190                     | 45             |
| antimony triacetate | 270                 | 90            | 190                     | 65             |
| antimony triacetate | 270                 | 120           | 190                     | 85             |
| antimony triacetate | 270                 | 150           | 190                     | 100            |
| antimony triacetate | 270                 | 180           | 190                     | 115            |
| antimony triacetate | 280                 | 30            | 190                     | 30             |
| antimony triacetate | 280                 | 60            | 190                     | 55             |
| antimony triacetate | 280                 | 90            | 190                     | 75             |
| antimony triacetate | 280                 | 120           | 190                     | 95             |
| antimony triacetate | 280                 | 150           | 190                     | 115            |
| antimony triacetate | 280                 | 180           | 190                     | 135            |
| tetrabutyl titanate | 280                 | 30            | 20                      | 45             |
| tetrabutyl titanate | 280                 | 60            | 20                      | 65             |
| tetrabutyl titanate | 280                 | 90            | 20                      | 85             |
| tetrabutyl titanate | 280                 | 120           | 20                      | 105            |
| tetrabutyl titanate | 280                 | 150           | 20                      | 125            |
| tetrabutyl titanate | 280                 | 180           | 20                      | 150            |

Further polycondensation reactions starting from bis-(2-hydroxyethyl)-  
5 terephthalate (BHET) were carried out in the glass equipment with screw  
mixer in presence of the catalysts 1 until 12.

- Catalyst of comparative example 1g : tributyltin (2-ethylhexanoate)
- Catalyst of comparative example 1h: dibutyltin bis(2-ethylhexanoate)
- Catalyst of comparative example 1i: monobutyltin tris (2-

10 ethylhexanoate)

- Catalyst of comparative example 1j: dibutyltin pinacolate
- Catalyst of comparative example 1k: monoocetylstannoic acid

- Catalyst of comparative example 1l: monobutylstannoic acid
- Catalyst of comparative example 1m: monoocetyltin tris(2-ethylhexanoate)
- Catalyst of comparative example 1n: monododecyltin tris(2-ethylhexanoate)

5 - Catalyst of example 3o: conversion product from monobutylstannoic acid with tetrabutyl titanate (4 Mol : 1 Mol)

- Catalyst of example 3p: conversion product from monoocetylstannoic acid with tetrabutyl titanate (1 Mol : 1 Mol)

10 - Catalyst of example 3q: conversion product from monoocetylstannoic acid with tetrabutyl titanate (4 Mol : 1 Mol)

- Catalyst of example 3r: conversion product from monobutylstannoic acid with tetrabutyl titanate (2 Mol : 1 Mol)

15 For the determination of the catalyst activity at first two concentrations of 20 ppm and 100 ppm were compared. The catalysts of (comparative) examples 1g through 1j were dissolved in toluene.

The catalysts were dissolved in dry toluene. The neat tin catalysts were  
20 used at a catalyst concentration of 40 ppm. The mixed catalysts (catalyst of examples 3o through 3q) were used at a tin content of 20 ppm. For the catalyst of example 3r the tin content of the catalyst was 22.9 ppm.

The tables 4a and 4b show the tin content and dosed catalyst amounts of  
25 the respective experiments.

BHET and the catalyst were introduced into the reaction vessel and rinsed well with nitrogen.

- 24 a-

The reaction vessel was placed into the salt bath. Recording of reaction time started now. Within 15 min the pressure was lowered from 100

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